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BRISTOL UNIV (ENGLAND) DEPT OF INORGANIC CHEMISTRY
TRANSITION METAL COMPOUNDS WITH POTENTIAL ELECTRONIC AND RADIAT--ETC(U)
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TRANSITION METAL COMPOUNDS WITH POTENTIAL
ELECTRONIC AND RADIATION RESISTANT PROPERTIES.

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10 September 1976

Final Scientific Report, 71 Aug 01 - 76 Jul 31.

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| 20. ABSTRACT (Continue on reverse side if necessary and identify by block number) Experimental work is reported involving the synthesis, properties, and structural characterisation of many new organometallic compounds. Cage structures containing boron, carbon and platinum are described, as are polynuclear metal clusters involving nickel, platinum and ruthenium. Especially novel discoveries include diplatinacarboranes, and tri- and tetra-nuclear nickel compounds with bridging acetylene and cyclooctatetraene groups. Studies on the activation of carbon-hydrogen, carbon-carbon, and carbon-halogen bonds using fluorocarbon reactants led to the isolation of numerous metalla-cyclic compounds. The | | | |

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Chemistry of sixteen electron molybdenum and tungsten complexes has been explored with particular reference to the activation of acetylenes. A bibliography of thirty three journal articles is appended.

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INTRODUCTION.

This report describes work carried out under Grant Number AFOSR-71-2090, and covers the period from August 1st 1971 through July 31st 1976. We have previously submitted through the European Office of Aerospace Research four Progress Reports as well as three Interim Scientific Reports dated September 17th, 1973, October 10th, 1974, and September 1st, 1975, respectively. The latter gave a summary of research carried out over the four year period, 71 Aug 01 - 75 Jul 31.

In addition to the Principal Investigator, the following persons have been associated with the research program for various periods of time during the five year period. Generally postdoctoral fellows worked with the group for one year or less whereas graduate students carried out research for longer periods. In the majority of cases stipends were provided by matching funds. Grant funds provided chemicals and other support.

Senior Research Personnel:[†] Drs. M. Green and S.A.R. Knox.

Junior Research Personnel:

| | |
|------------------|----------------|
| G.K. Barker* | B.L. Goodall |
| R.L. Bennett | J.A.K. Howard* |
| D.H. Bowen* | A.C. Laguna* |
| Miss J. Browning | P.K. Maples* |
| W.E. Carroll* | R.P. Phillips |
| J. Clemens | G. Shaw* |
| C.H. Davies | B. Sosinsky |
| J.L. Davidson* | J.L. Spencer* |
| C.H. Game | B.F. Taylor* |
| R.C.F. Gardner | B.J. Thomson* |
| R.D. George* | A.J. Welch* |

* Postdoctoral Research Assistants. † Dr. M.I. Bruce was associated with some aspects of the research until his departure in 1973 to become professor of chemistry at Adelaide, Australia.

RESEARCH ACCOMPLISHED.

As was stated in the Third Interim Scientific Report (September 1975), our researches can be classified under the main headings of (i) Polynuclear complexes, and (ii) Chemical activation of small molecules by metal complex formation.

In terms of research publications, the work has been very successful since thirty three (33) primary journal articles describing research supported in part by this Grant have either been published or have been submitted for publication during its five year period. Because of this very large volume of work, all of the results will not be discussed in detail in this Report. Instead, only highlights of the research will be mentioned. References to the relevant publications will be given in the cursive text according to their numbers on the list^{*} so that the interested reader will be able to seek additional details by consulting the original journal articles.

POLYNUCLEAR METAL COMPLEXES.

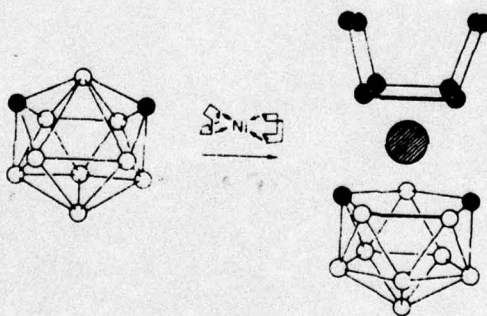
Research on metal complexes having cluster or cage-like structures is important in the context of the search for new materials expected to display useful conductivity, optical, or thermal stability. We have discovered several new syntheses of polynuclear compounds, a field of research which continues to be under very active study in many laboratories throughout the world

(i) Metallacarborane Clusters.

During the course of our research program we developed a new approach to the synthesis of the metallacarboranes (compounds containing aggregates of metal, carbon and boron atoms) based on the direct reaction of low

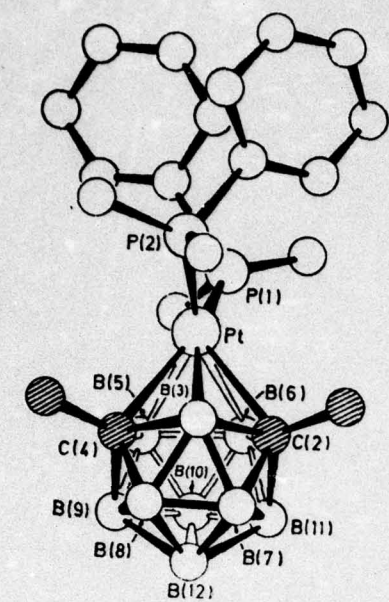
* See page 20 for list of references.

valent transition metal complexes with a carborane.^{8,18,19,20,23,25,26,27} Molecular structures of many of the compounds were elucidated by single crystal X-ray diffraction studies. Some of the more novel structures are shown in Figures 1 - 8. The new synthetic approach was first employed using 11-atom carboranes where it was shown that reaction of these species with a d^{10} complex of nickel, palladium or platinum resulted in a direct insertion of the metal atom into the cage (see Scheme 1 illustrating reaction between $[\text{Ni}(\text{C}_8\text{H}_{12})_2]$ and $\text{C}_2\text{B}_9\text{H}_{11}$). The resulting structures were of the closo-type, and the method of synthesis could be extended to mono-carbon carboranes and to metallacarboranes with 11-vertex structures, the latter affording clusters containing two different transition metals (2). These reactions formally involve a net transfer of electrons from the metal to the cage, representing an important new aspect of oxidative-addition chemistry.



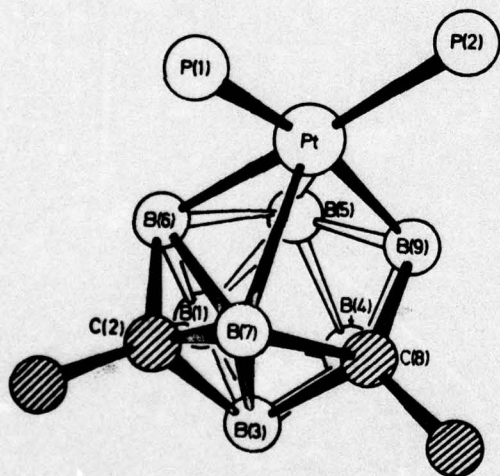
Scheme 1.

When the direct oxidative-insertion reaction was extended to carboranes containing less than eleven vertices the new compounds were found to display unusual structural features. For example, instead of closo-structures being uniformly produced the new species often possessed nido-structures (a polyhedron with one vertex removed) rather than closo, and the inserted metal atom, usually platinum, showed a marked



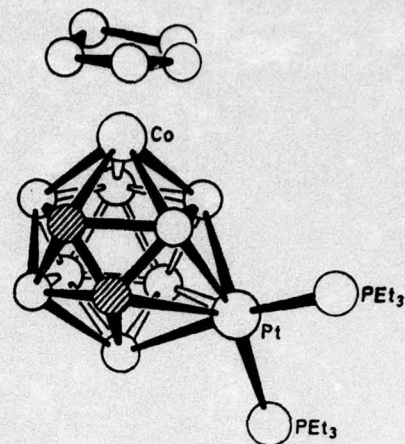
General view of the molecule
1,1-(PhMe₂P)₂-2,4-Me₂-1,2,4-PtC₂B₈H₈

1



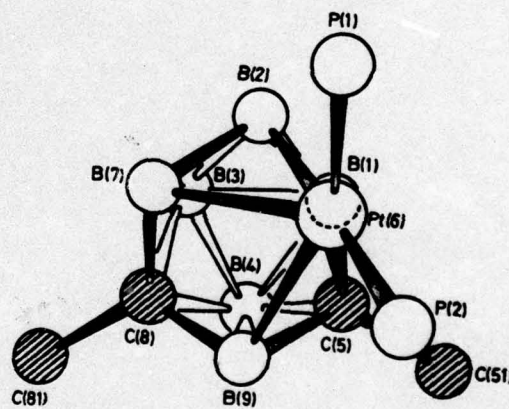
Structure of [Me₂C₂B₇H₇]Pt[PEt₃]₂. Phosphino ethyl groups are omitted for clarity.

3



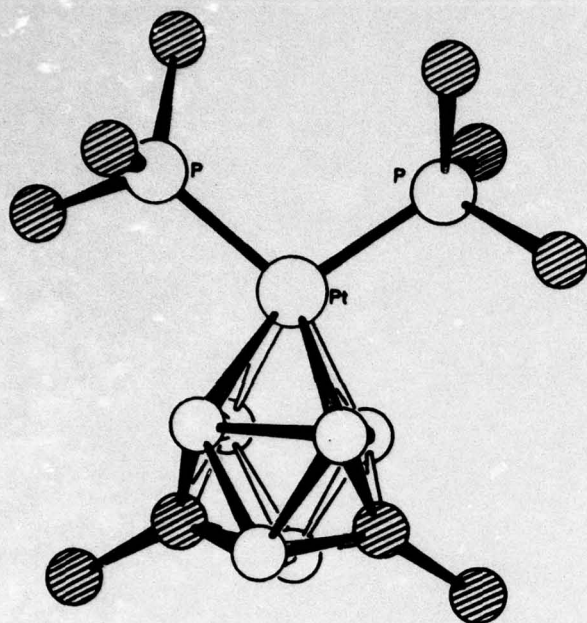
General view of the molecule
1-(7-C₆H₅)-8,8-(Et₃P)₂-1,2,7,8-CoC₂PtB₈H₁₀

2



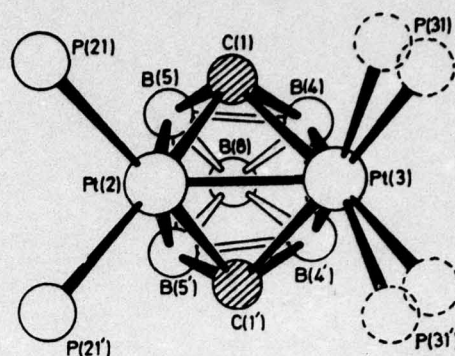
nido-6,6-(Et₃P)₂-5,8-Me₂-6,5,8-PtC₂B₈H₈

4



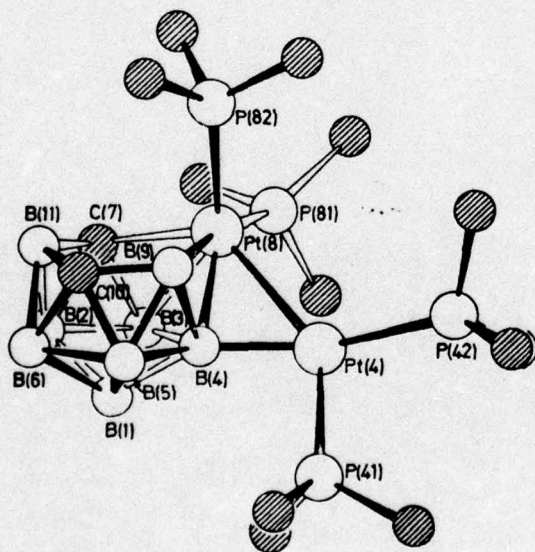
closo-1,1-(Me₃P)₂-6,8-Me₂-1,6,8-PtC₂B₆H₆.

5



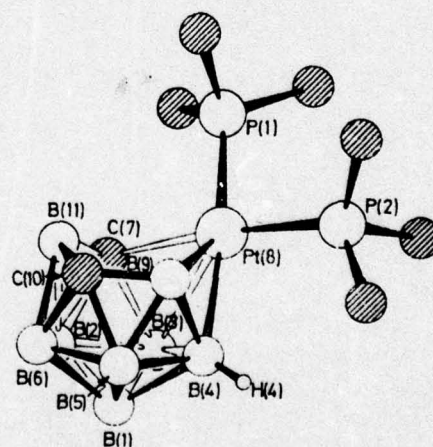
Molecular structure of *closo*-2,3-[(Et₃P)₂]₂-1,2,3,6-CPt₂CB₆H₆. Phosphinoethyl groups are omitted for clarity.

6



Molecular structure of *nido*-μ(4,8)-[(Me₃P)₂Pt]₂-8,8-(Me₃P)₂-7,8,10-CPtCB₆H₁₀.

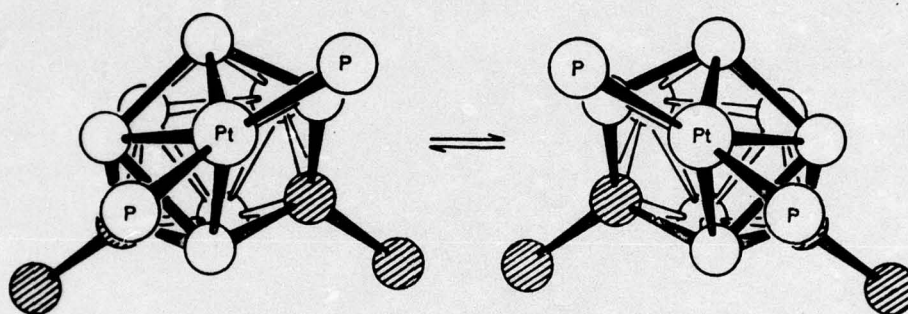
7



Molecular structure of *nido*-8,8-[(Me₃P)₂]₂-7,8,10-CPtCB₆H₁₀.

8

preference to bond to the boron atoms of the cage in preference to the carbon. Thus 3 illustrates the nido-cluster complex obtained from $[\text{Pt}(\text{Et}_3\text{P})_3]$ and $\text{Me}_2\text{C}_2\text{B}_7\text{H}_7$, and 4 a nido-metallacarborane prepared by reacting $[\text{Pt}(\text{trans-stilbene})(\text{Et}_3\text{P})_2]$ with $\text{Me}_2\text{C}_2\text{B}_6\text{H}_6$. The important and interesting observation was made that in solution the compound $[\text{Pt}(\text{Me}_2\text{C}_2\text{B}_7\text{H}_7)(\text{Et}_3\text{P})_2]$ underwent a rapid degenerate rearrangement (Scheme 2) as detected by ^{11}B and ^{31}P n.m.r. studies.



Scheme 2.

The complex 5, prepared by reacting closo-1,6- Me_2 -1,6- $\text{C}_2\text{B}_6\text{H}_6$ with $[\text{Pt}(\text{trans-stilbene})(\text{Me}_3\text{P})_2]$, represents the first structurally authenticated example of a boracyclobutadiene derivative, the isolation and characterisation of which has served to emphasize further the wide scope of metallacarborane chemistry.

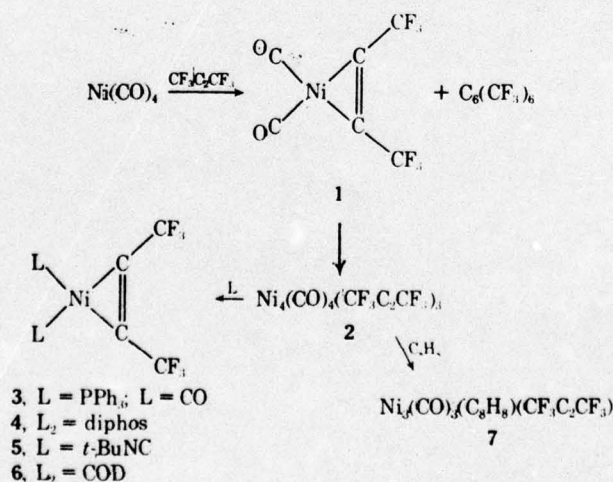
Whereas direct insertion of d^{10} Ni, Pd or Pt species into 8-, 9- and 11-atom closo-carboranes led to the discovery of a new approach to the synthesis of both closo- and nido-metallacarboranes, analogous reactions with 7- and 10-atom carboranes gave hitherto unknown types of bimetallic species. Thus reaction of closo-2,4- $\text{C}_2\text{B}_5\text{H}_7$ with $[\text{Pt}(\text{styrene})(\text{Et}_3\text{P})_2]$ gave 6, whereas $[\text{Pt}(1,5\text{-C}_8\text{H}_{12})(\text{Me}_3\text{P})_2]$ and 1,6- $\text{C}_2\text{B}_8\text{H}_{10}$ gave the very novel structure 7. Treatment of the latter with charcoal afforded 8. Structure 7 with one metal atom within the cage and the other

without, is without precedent in inorganic cluster chemistry.

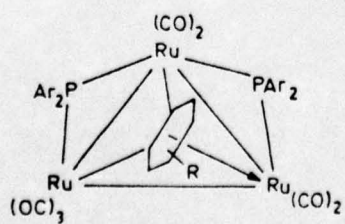
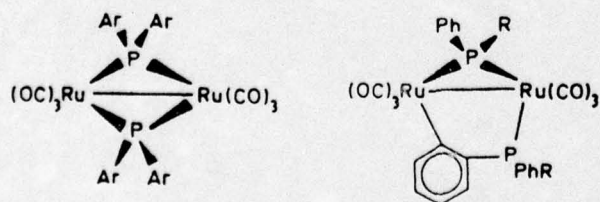
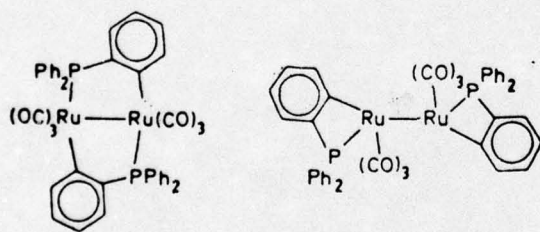
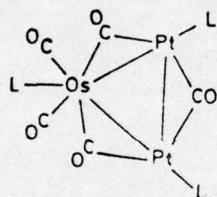
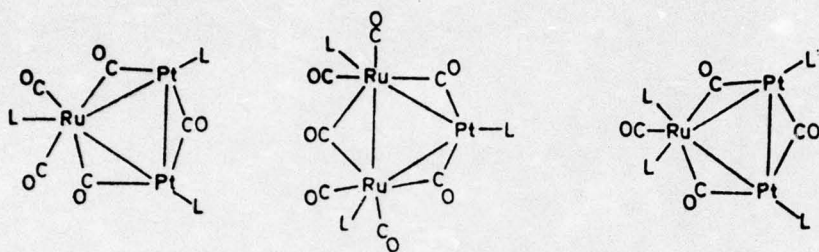
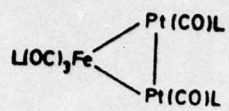
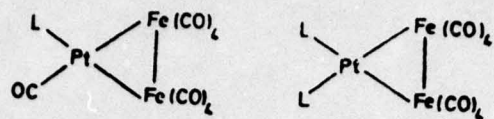
Some reactions between zero-valent complexes of nickel, palladium and platinum with arachno-carboranes were also investigated. Arachno structures are based on polyhedra with two vertices missing, and in carborane chemistry one example of such a structure is that of $\text{Me}_2\text{C}_2\text{B}_7\text{H}_{11}$. Reaction of the latter with, for example, $[\text{Ni}(\text{C}_8\text{H}_{12})(\text{Et}_3\text{P})_2]$ gives the nido-compound $[6,6-(\text{Et}_3\text{P})_2-5,9-\text{Me}_2-6,5,9-\text{NiC}_2\text{B}_7\text{H}_9]$, a cluster in which a nickel atom is attached to a B_2C -system in a 1,2,3- η bonding mode.²⁶

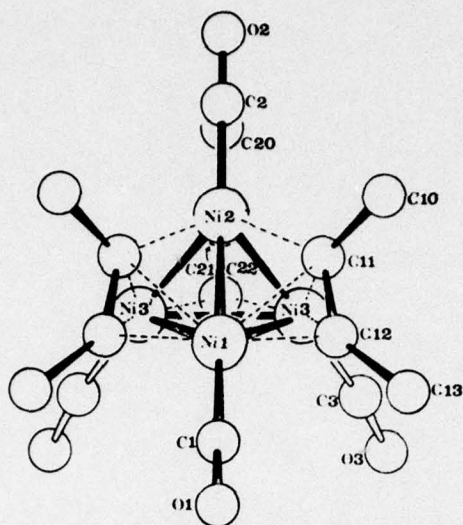
(ii) Polynuclear Metal Carbonyl Complexes.

It has long been known that transition metals have a strong tendency to form metal-metal bonds in their carbonyl derivatives. Even though this is now a relatively old field of study important discoveries continue to be made. Early in the Grant period we characterised^{1-3,10} several unusual cluster compounds of platinum and ruthenium shown on page 8 of this Report. Recently, in the Journal of the American Chemical Society,²⁸ we have described two nickel atom clusters of special novelty (9, 10) (page 9). These compounds were prepared by the reactions illustrated in Scheme 3.



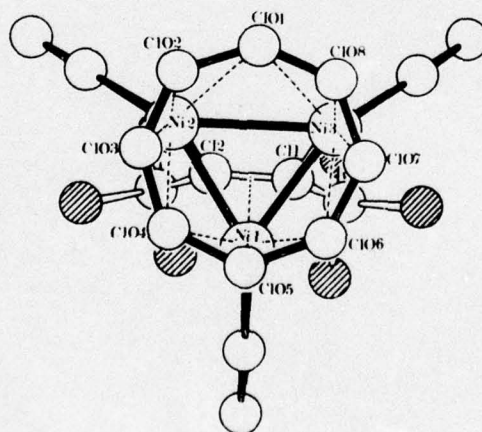
Scheme 3.





Molecular structure of $[\text{Ni}_4(\text{CO})_4(\text{CF}_3\text{C}_2\text{CF}_3)_3]$. Fluorine atoms omitted for clarity. The Ni-CO bond distances average 1.81 (6) Å and the three Ni(apex)-Ni(basal)-CO fractions are each nearly linear. The three OC-Ni(apex)-Ni(basal) are each nonlinear with the OC-Ni(apex) vector nearly collinear with the idealized C_3 axis of the molecule.

9



Molecular structure of $[\text{Ni}_3(\text{CO})_3(\text{C}_8\text{H}_8)(\text{CF}_3\text{C}_2\text{CF}_3)]$. The Ni-CO distances average 1.78 (1) Å, with the carbonyl groups bent ca. 30° out of the Ni_3 plane away from the C_8 ring.

10

The tetranuclear nickel species 9 is the first example of a large class of $[M_4L_4(\mu_X(\eta^2)-L')_3]$ clusters, * while the trinuclear nickel cluster provides the first example of a polynuclear metal complex in which a planar cyclooctatetraene ring bridges three metal atoms as it might on the surface of a metal. These two compounds are of considerable interest within the context of those cluster complexes which are fluxional and chemically active in relation to their ability to provide multinuclear sites for the bonding of alkenes or alkynes.

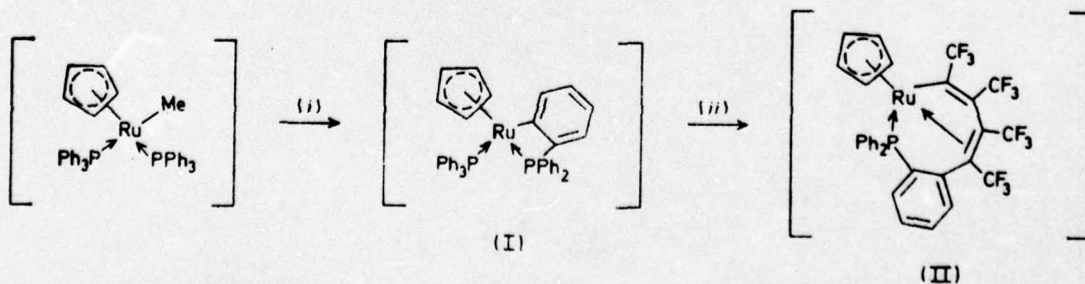
CHEMICAL ACTIVATION OF SMALL MOLECULES BY COMPLEX FORMATION.

In the search for new catalyst systems relevant to polymer and petrochemicals fundamental information is required concerning the ability of transition metals to activate chemically C-H, C-X (X = halogen) or C-C bonds. Our researches have been conducted in three main areas:

(i) Cyclo-metallation and related reactions, (ii) Fluoro- and chlorofluoro-carbon-metal complexes, and (iii) Sixteen-electron complexes of molybdenum and tungsten.

(i) Cyclo-metallation and Related Reactions.

In the early stages of our research^{4,13,21} we were involved in the study of ortho-metallation reactions relating to the activation of C-H bonds by metals. For example, Scheme 4 illustrates the reactivity towards acetylenes of an ortho-metallated compound (I) to give a novel heterocyclic complex (II).



Scheme 4.

(i), Refluxing decalin, -CH₂; (ii), C₂(CF₃)₂

* M.G. Thomas, E.L. Muetterties, R.O. Day and V.W. Day, J.Amer.Chem.Soc., 1975, 98, 4645. .

More recently²⁹ ortho-metallation reactions of several η^5 -cyclopentadienylruthenium complexes have been investigated in detail leading, inter-alia, to the characterisation of the metallo-cycles shown in Scheme 5.

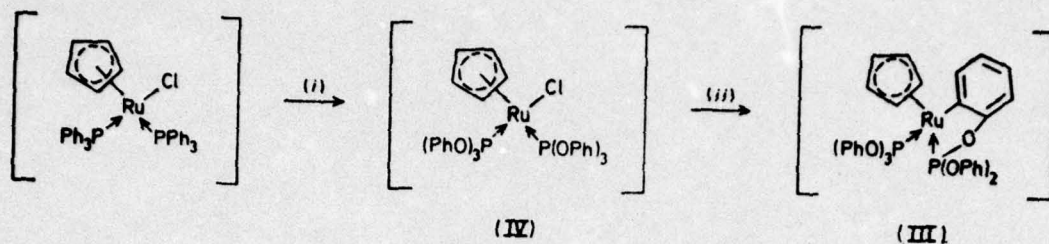
(ii) Fluoro- and Chlorofluorocarbon-metal Complexes.

The study of fluorocarbon-metal complexes has been useful in providing models for the ways in which analogous hydrocarbons may react with transition metal compounds. It is often possible to isolate and study reaction intermediates when fluoro- or chlorofluoro-carbon compounds are employed as substrate molecules in reactions with reactive organometallic compounds, whereas the same is frequently not possible when the analogous hydrocarbons are used.

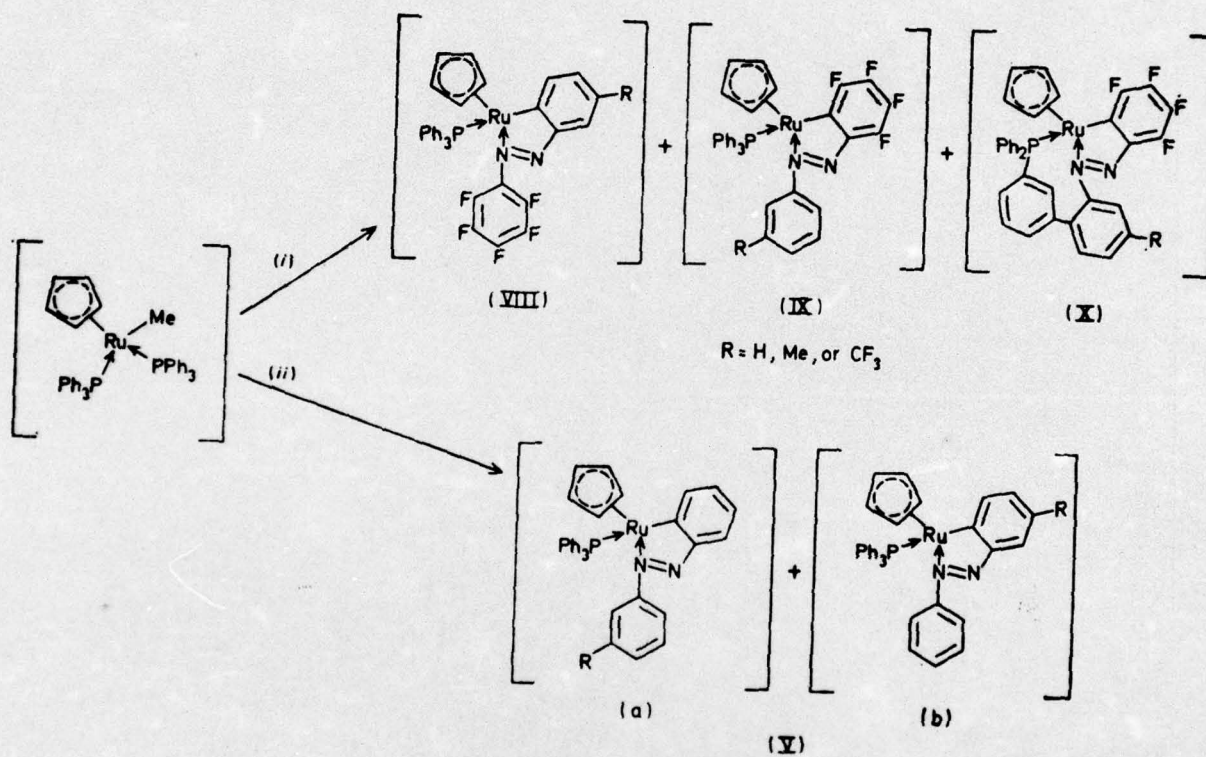
In references 5-7, 12, 14, 15 and 24 we describe numerous new fluorocarbon-metal complexes formed by C-C, C-O or C-N bond formation within the coordination sphere of a metal, with concomitant synthesis of carbon-metal bonds. These studies involved metal complexes of ruthenium, cobalt, iridium, nickel, palladium and platinum. The scope of our activity in this area is demonstrated by the compounds listed on page 13.

We have also discovered^{11,17} a series of tin halide promoted rearrangement reactions of coordinated fluorocarbons, in which C-F bonds are "activated" and converted into C-Cl or C-Br linkages (Scheme 6). In the absence of a metal centre this type of reaction does not occur.

Recently³¹ we have extended our work with fluorocarbon-metal complexes to a study of insertion reactions of hexafluorobut-2-yne, tetrafluoroethylene, and hexafluoroacetone with cyclopentadienyl-iron, -ruthenium, -palladium and -molybdenum complexes. In this manner we have discovered many new compounds, the structures of which are shown



(i), P(OPh)_3 ; (ii), refluxing decalin, $-\text{HCl}$

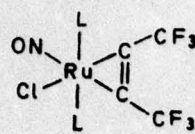


R = H, Me, or CF_3

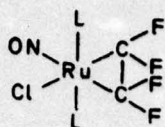
R = H, Me, OMe, CO_2Et , or CF_3

(i), $m\text{-RC}_6\text{H}_4\text{N}=\text{NC}_6\text{F}_5$; (ii), $m\text{-RC}_6\text{H}_4\text{N}=\text{NPh}$

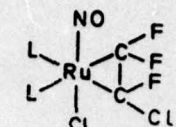
Scheme 5.



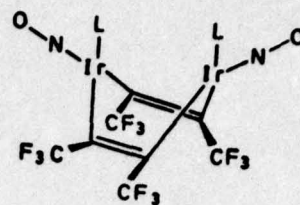
(II) L = PPh₃
(VI) L = PMePh₂
(IX) L = PMe₂Ph



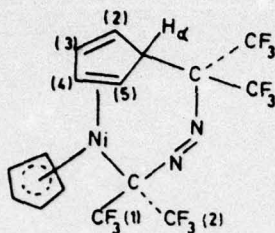
(III) L = PPh₃
(VII) L = PMePh₂
(X) L = PMe₂Ph



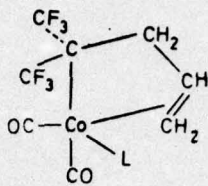
(XI) L = PMe₂Ph



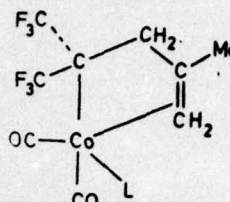
(XIV) L = PPh₃



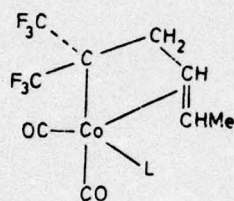
(I)



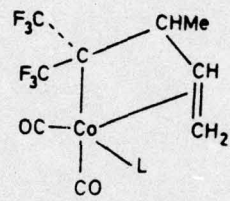
(II, L = CO)
(V, L = PPh₃)
(VI, L = AsPh₃)



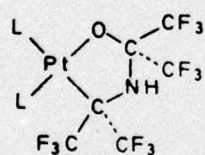
(III, L = CO)
(VII, L = PPh₃)
(VIII, L = AsPh₃)



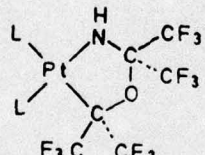
(IXa, L = CO)
(IX, L = PPh₃)
(X, L = AsPh₃)



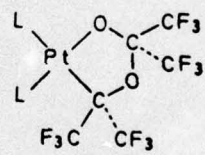
(IVb, L = CO)



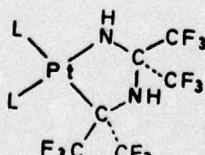
(Ia) L = PPh₃
(IIIa) L = PMePh₂



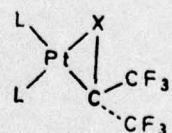
(Ib) L = PPh₃
(IIIb) L = PMePh₂



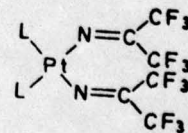
(II) L = PMePh₂
(V) L₂ = Ph₂PCH₂CH₂PPh₂
(IX) L = P(OMe)₃
(XI) L₂ = 1,5-C₈H₁₂



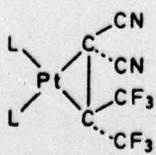
(VII) L₂ = Ph₂PCH₂CH₂PPh₂



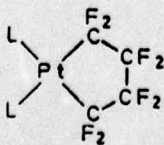
(IV) L₂ = Ph₂PCH₂CH₂PPh₂, X = O
(VI) L₂ = Ph₂PCH₂CH₂PPh₂, X = NH
(VIII) L = P(OPh)₃, X = O



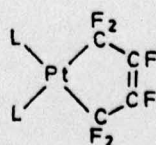
(XV) L₂ = 1,5-C₈H₁₂



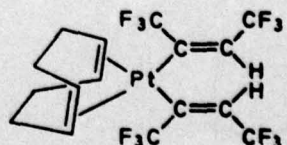
(XII) L₂ = 1,5-C₈H₁₂



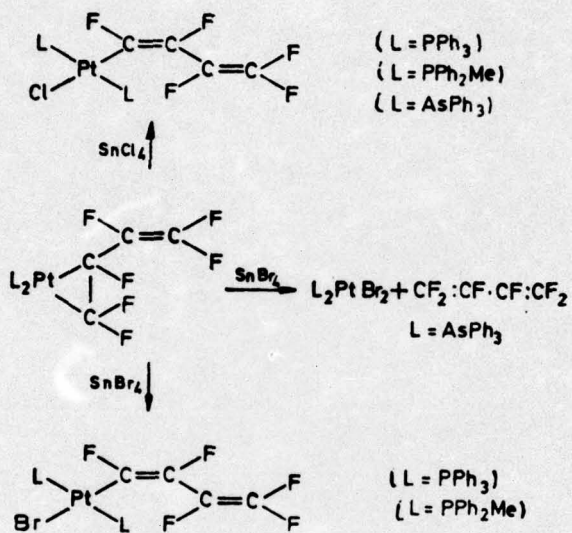
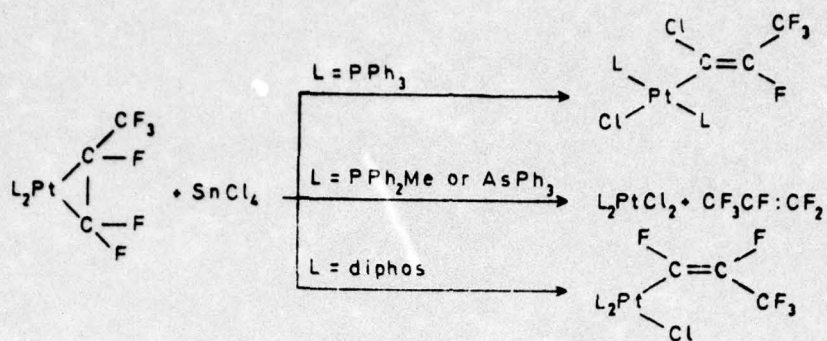
(X) L₂ = 1,5-C₈H₁₂



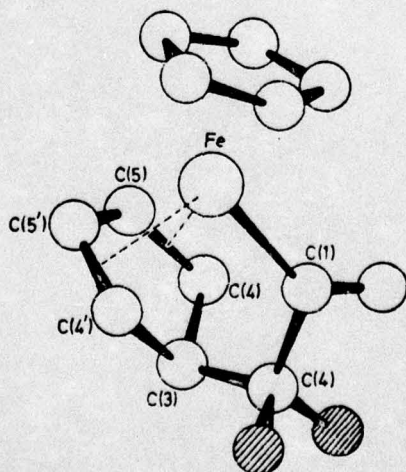
(XIII) L₂ = 1,5-C₈H₁₂



(XIV)



Scheme 6.



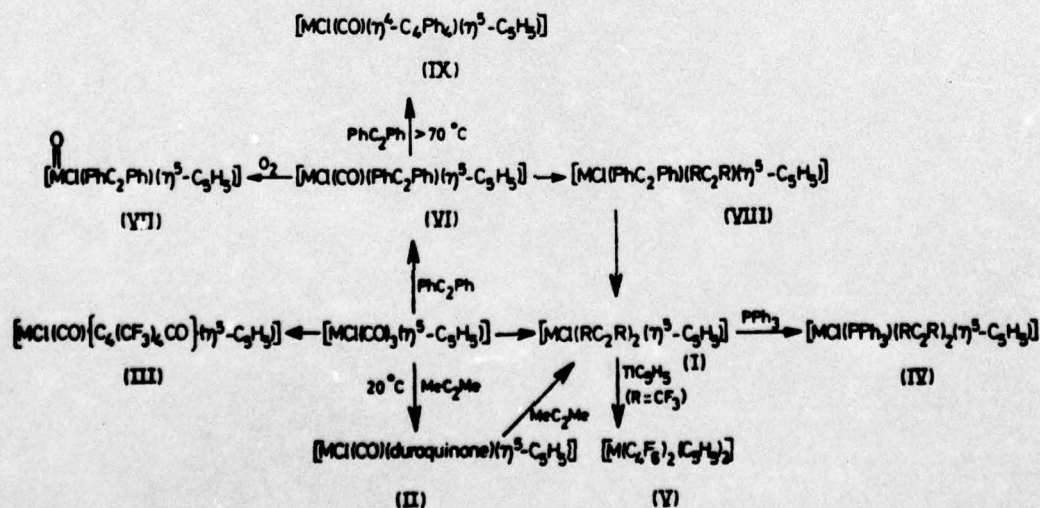
The complex $[\text{Fe}(\text{COCF}_2\text{C}_6\text{H}_5)(\eta^4\text{-C}_6\text{H}_5)]$. Fe-C(1), 1.99(1); Fe-C(4), 2.18(2); Fe-C(5), 2.06(2); and C(3)-C(4), 1.64(2) Å. The $\eta^4\text{-C}_6\text{H}_5$ ring has an envelope conformation with an acute folding angle of 25.4°.

on page 16. A number of new insertion reactions have been identified. A particularly novel result was the characterisation of complex 11 (XII on page 16), formed by the apparent cleavage of the C=C double bond in C_2F_4 .

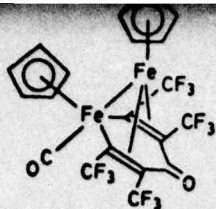
(iii) Sixteen Electron Complexes of Molybdenum and Tungsten.

Organometallic chemistry is dominated by compounds which obey the 18-electron rule. In these complexes all the metal bonding orbitals are occupied and the species are kinetically stable, reacting only by ligand dissociation, processes which generate a vacant site. Of potential interest, from the chemical reactivity point of view, are 16-electron complexes which have vacant coordination sites to which substrate molecules can become bonded as a prelude to chemical reaction via modification of their bonding properties by interaction with metal orbitals. In the case of an organic reactant this can take the form of C-H or C-C bond activation. During our researches we have investigated the chemistry of new 16-electron complexes of molybdenum and tungsten.³⁰⁻³²

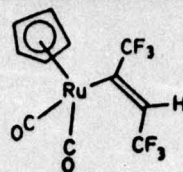
Reaction of $[MCl(CO)_3(\eta^5-C_5H_5)]$ ($M = Mo$ or W) with acetylenes affords the 16-electron species $[MCl(RC_2R)_2(\eta^5-C_5H_5)]$, which were structurally characterised by X-ray crystallography, and shown to react with donor ligands and with TlC_5H_5 (Scheme 7). These compounds are thus highly reactive.



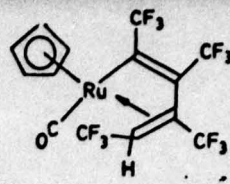
Scheme 7.



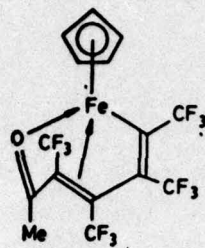
(I)



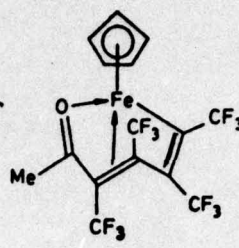
(II)



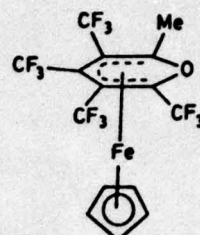
(III)^a



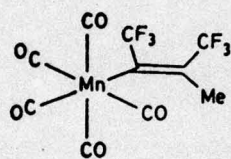
(IVa)



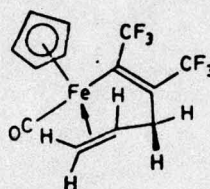
(IVb)



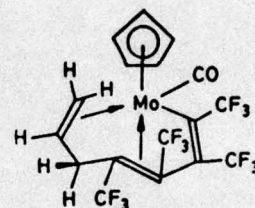
(IVc)



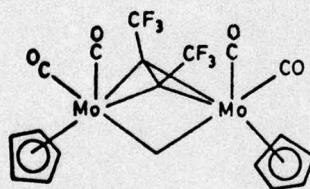
(V)



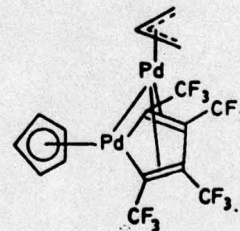
(VI)



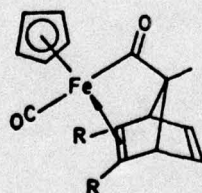
(VII)



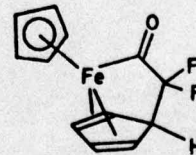
(VIII)



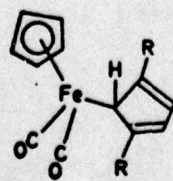
(IX)



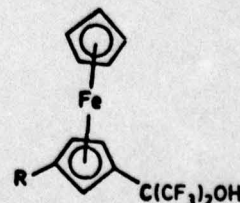
(X) R=CF₃
(XI) R=CO₂Me



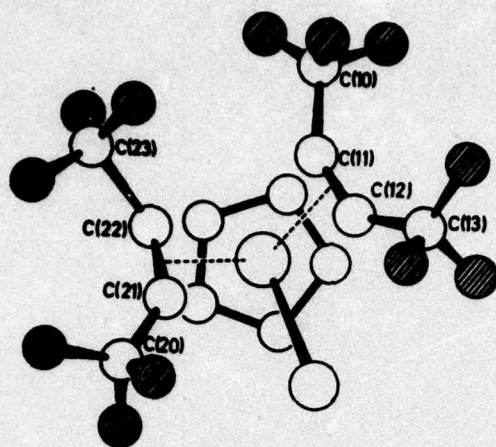
(XII)



(XIII) R=C(CF₃)₂OH

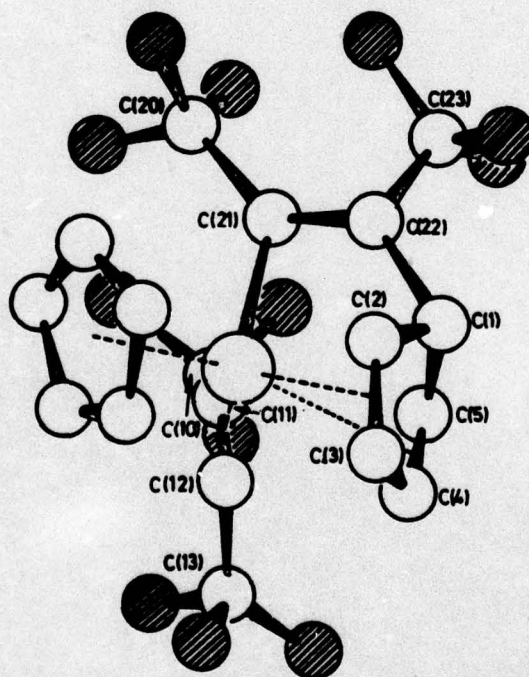


(XIV) R=C(CF₃)₂OH
(XV) R=H



Molecular structure of $[W(Cl)(CF_3C_6CF_3)_3(\eta^4-C_6H_6)]$.

12



Molecular structure of $[Mo(CF_3C_6CF_3)_3(\eta^4-C_6H_6) \cdot C(CF_3)_3 \cdot C(CF_3)_3]$

13

The molecular structure of the 16-electron tungsten complex

$[\text{WCl}(\text{CF}_3\text{C}_2\text{CF}_3)_2(\eta^5\text{-C}_5\text{H}_5)]$ is shown in 12, (page 17).

The extensive chemistry of the species $[\text{MCl}(\text{CF}_3\text{C}_2\text{CF}_3)_2(\eta^5\text{-C}_5\text{H}_5)]$ was further demonstrated by reactions with TiSC_6F_5 to give compounds $[\text{M}(\text{SC}_6\text{F}_5)(\text{CF}_3\text{C}_2\text{CF}_3)_2(\eta^5\text{-C}_5\text{H}_5)]$; the related species $[\text{M}(\text{SC}_6\text{F}_5)(\text{CO})(\text{PhC}_2\text{Ph})(\eta^5\text{-C}_5\text{H}_5)]$ being similarly obtained from $[\text{MCl}(\text{CO})(\text{PhC}_2\text{Ph})(\eta^5\text{-C}_5\text{H}_5)]$. Cyclopentadienylthallium reacts with the compounds $[\text{MCl}(\text{CF}_3\text{C}_2\text{CF}_3)_2(\eta^5\text{-C}_5\text{H}_5)]$ to afford insertion products $[\text{M}\cdot\text{C}(\text{CF}_3)_2:\text{C}(\text{CF}_3)_2\cdot\text{C}_5\text{H}_5(\text{CF}_3\text{C}_2\text{CF}_3)(\eta^5\text{-C}_5\text{H}_5)]$; the molybdenum compound being characterised by a single crystal X-ray diffraction study (13).

The molybdenum compound $[\text{MoCl}(\text{CF}_3\text{C}_2\text{CF}_3)_2(\eta^5\text{-C}_5\text{H}_5)]$ underwent an unusual reaction with the tris(pyrazolyl)borate anion giving a complex containing no boron but an η^3 -allyl group, linking two pyrazole ligands and formed by condensation of the two hexafluorobut-2-yne ligands originally coordinated to the metal. Buta-1,3-diene reacted with $[\text{MoCl}(\text{CF}_3\text{C}_2\text{CF}_3)_2(\eta^5\text{-C}_5\text{H}_5)]$ to give $[\text{MoCl}_2(\eta^4\text{-C}_4\text{H}_6)(\eta^5\text{-C}_5\text{H}_5)]$ and with $[\text{MoCl}(\text{CO})(\text{PhC}_2\text{Ph})(\eta^5\text{-C}_5\text{H}_5)]$ to yield the same compound or $[\text{MoCl}(\text{CO})(\eta^4\text{-C}_4\text{H}_6)(\eta^5\text{-C}_5\text{H}_5)]$, depending on the solvent. The tungsten compound $[\text{WCl}(\text{CO})(\eta^4\text{-C}_4\text{H}_6)(\eta^5\text{-C}_5\text{H}_5)]$ was also prepared. Reactions of bicyclo[2.2.1]heptadiene with the compounds $[\text{MCl}(\text{CF}_3\text{C}_2\text{CF}_3)_2(\eta^5\text{-C}_5\text{H}_5)]$ were also studied.

SUMMARY OF RESULTS ACHIEVED.

Advances have been made in two main areas of organometallic chemistry:

(a) Polynuclear metal complexes, and (b) Chemical activation of small molecules by metal complex formation.

(a) New metal-cage structures containing nickel, palladium or platinum atoms have been prepared by polyhedral expansion of carboranes with zero-valent complexes of these metals. Entirely new structural types have

been identified for the first time including a diplatinum complex in which one metal atom is located within the cage of boron and carbon atoms while the second is external to the cage but joined to it by a Pt-Pt and a Pt-B bond. In another area of metal cluster chemistry several polynuclear carbonyl compounds of ruthenium and platinum have been characterised, as have two novel nickel complexes

$[\text{Ni}_4(\text{CO})_4(\mu_3\text{-CF}_3\text{C}_2\text{CF}_3)_3]$ and $[\text{Ni}_3(\text{CO})_3(\mu_3\text{-C}_8\text{H}_8)(\mu_3\text{-CF}_3\text{C}_2\text{CF}_3)]$. In the latter a planar C_8 ring bridges a nickel triangle, whereas in the former structure three acetylene ligands bridge faces of a Ni_4 tetrahedron.

(b) Several new cyclometallation reactions have been identified, particularly involving the group $[\text{Ru}(\text{Ph}_3\text{P})(\eta^5\text{-C}_5\text{H}_5)]$ and azobenzene derivatives. Numerous fluorocarbon metal complexes have been prepared by oxidative-addition reactions of d^8 and d^{10} metal compounds. The activation of carbon-fluorine bonds towards substitution by chlorine or bromine has been demonstrated for fluoro-olefin metal complexes. Novel insertion products have been obtained by reacting hexafluoro-but-2-yne, tetrafluoroethylene and hexafluoroacetone with cyclopentadienyl-iron, -ruthenium, -palladium and -molybdenum complexes. A detailed study has been made of the chemical reactivity of the 16-electron complexes $[\text{MCl}(\text{CF}_3\text{C}_2\text{CF}_3)_2(\eta^5\text{-C}_5\text{H}_5)]$ ($\text{M} = \text{Mo}, \text{W}$).

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4. Metallation and Related Reactions with π -Cyclopentadienyl-ruthenium Complexes.
by M.I. Bruce, R.C.F. Gardner and F.G.A. Stone, J.Organometal.Chem. 1972, 40, C39.
5. Reactions of Low-Valent Metal Complexes with Fluorocarbons. Part XXIV. Chloronitrosylbis(triphenyl-, methyldiphenyl- and dimethylphenyl-phosphine)ruthenium and Nitrosyl(triphenylphosphine)iridium.
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10. Triaryl Phosphite Derivatives of Dodecacarbonyltriruthenium.
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11. Lewis Acid Promoted Vinyl-rearrangement and Halogen-exchange of Platinum-fluoroolefin Complexes.
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19. Formation of closo- and nido-Metallocarboranes from closo-C₂B₉ and -C₂B₇ Carboranes; Molecular Structures of closo-1,1-(Me₂PhP)₂-2,4-Me₂-1,2,4-PtC₂B₉H₉ and nido-10,10-(Et₃P)₂-2,8-Me₂-10,2,8-PtC₂B₇H₇.
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